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Novel Methods for Binding Disparate Materials

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Disclaimer

Auspices Statement

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Abstract

This project was intended to advance the science of surface bonding in order to provide the functionality demanded by target fabrication requirements, as well as similar needs in other fields of importance to LLNL. We have developed and demonstrated a very powerful capability, i.e. "single molecule force spectroscopy," that allows the strength of individual chemical bonds to be measured. This project focused on long chain molecules that are covalently bound to surfaces on one end and have complementary reactive groups that have the potential for bridging between surfaces. In biological systems, long chain tethers provide the mechanism for adhesion between dissimilar surfaces, e.g. bacteria adhesion to cells, and were found useful for developing the methodology. Polymer tethers offer the means to bridge across finite surface roughness and have the potential of forming thin, well-characterized bonds on a variety of surfaces

Introduction/Background

An extremely thin, but still robust, bond is an identified need for many applications. Surfaces of different materials can often be coated to provide chemical compatibility between the surfaces or between a bonding agent and the two surfaces, but normally only a limited number of points on surfaces will contact each other unless the bonding agent is supplied in quantities large enough to fill the gaps. A key goal of this project was to determine the tether length necessary to span a specific gap between the surfaces of two different materials in order to produce a bonding agent (or strategy) that applied as a monolayer of molecules would form a bond of limiting thickness. Four steps are involved in this effort: 1) determining the RMS roughness of the relevant materials using an AFM (quartz, sapphire, aluminum, titanium), 2) functionalizing both an AFM tip and a substrate with end-active polymers, 3) using force spectroscopy methods to determine the strength of individual bonds, and 4) measuring the frequency of adhesion events as a function of the AFM tip distance and polymer length when surface roughness is replicated by holding the AFM tip above the substrate at the RMS roughness value.

Research Activities and Results

1) **Measuring the RMS roughness of relevant materials**

The roughness of the quartz and the sapphire were both approximately 2-3 nm RMS over ~ 400 micron^2 areas, and standard glass cleaning protocols were enough to remove most dust and other contaminants. This was not true however for the diamond-turned aluminum as determined using an AFM. Although the RMS roughness for the aluminum was comparable to the quartz and sapphire windows (~3-5 nm RMS over ~ 600 micron^2 areas) the surfaces were heavily contaminated with small roughly hemispherical particles ~40 -400 nm in diameter and 10-60 nm in height. These particles could not be removed by any standard solvent washes or by applying shear forces of ~700 nanoNewtons with an AFM tip. From discussions scientists in Precision Engineering it was determined that these particles are probably aluminum tailings from the surface machining and are welded in place.

2) **Functionalizing AFM tips and substrates with end-active polymers**

This project has made LLNL leaders in the field of force spectroscopy largely because of the ability to reproducibly functionalize AFM tips. The silane chemistry utilizied to derivitize surfaces will work well on any anti-reflective (AR) coated surface and novel thiol chemistries were investigated for binding to gold surfaces.

Some quite surprising observations were made involving thiol chemistries for attachment. The rupture force experiments with thioctic acid derivatized probes gave results showing that the force required to break the interaction of this dithiane with the gold surface is substantially less than that required to break a simple thiol-Au bond. It is generally expected that if two independent non-interacting Au-S bonds were to be broken simultaneously then twice the force necessary to rupture one Au-S bond would be needed to break two Au-S bonds. However, applying force to a system where the two sulfur atoms on one molecule are spatially constrained, a situation apparently develops in which a pericyclic reaction occurs and Au-S bond breaking happens simultaneously, or in synchronicity, with S-S bond formation, thereby precluding the generation of high energy active intermediates with the result being a much lower activation energy for the displacement reaction.

3) **Measuring the frequency of adhesion events as a function of the distance between the tip and the substrate and polymer length (hovering tip experiments)**

Experiments were performed using end-active polymers attached to AFM tips to measure the gaps over which polymers can stretch and bind. Figure 1 shows a representative experiment demonstrating the process. A polymer-functionalized AFM tip is lowered toward a polymer-functionalized substrate in small 5 nm increments. The tip is maintained at each fixed distance for 2 minutes (hovering), long enough for the polymer to explore its entire reaction volume ~1.2e10 times. As the tip hovers, the lateral deflection of the cantilever is monitored and when bonding occurs the signal is heavily damped. The tip-sample distance is monitored and correlated with the frequency of bond formation.

It was found that in polar solvents, ~25 nm long polymers attached to both surfaces can bridge ~20 nm gaps between those surfaces almost 100% of the time. However, earlier results indicated that using non-polar solvents resulted in greater extensions of the polymer tethers. Figure 2 shows force curves of polymer extensions taken in a non-polar solvent. By fitting these curves with a model that includes the polymer stiffness, it has been shown that in nonpolar solvents polyethelene glycol (PEG) tethers are ~16 times stiffer than in polar solvents. These results in conjunction with the earlier data indicate that the volumes that the polymers sweep out can be tailored to the specific bonding requirements, i.e. surface roughness, by controlling the solvent polarity. An issue to be addressed however is that if the polymer stiffness increases, the diffusion rate of the functional endgroup of the polymer should decrease. This implies that it will take longer for the polymer to explore its volume, find the other polymer, and form a bond. Hovering tip experiments to examine the interplay between bond formation frequency and solvent polarity in order to determine the correct solvents to use.

Exit Plan

The force spectroscopy method is now being used in DNT to study aging of materials and in NAI to study the adhesion of viruses in mass spectroscopy system designed to identify viruses in biosecurity applications. Two members of this team were also involved in the cancer detection work described on the front page of Newsline. It is possible that this work could be continued through support by the National Institutes of Health.

Summary

AFM tips derivatized with small numbers of chemically active molecules tethered to the tip by a polymer chain can be used to probe the properties of surfaces and to identify features of an object's surface with extremely high chemical specificity. The tether allows the specific bond between the active molecule and its target molecule to be studied independent of non-specific forces. Tethering of molecules to the AFM tip also allows exploration of the behavior of the tether under different conditions including changes in solvent as was explored here.

References

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INVITED TALKS:

"Probing Intermolecular Interactions Using Single-molecule Force Spectroscopy-Biophysics Seminar," UC Davis, March, 2004.

"Studying Molecular Interactions with Force Spectroscopy," LANL, May 13, 2004.

CONTRIBUTED TALKS:

"Mono and Multivalency in Tethered Protein-Carbohydrate Bonds,"
227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004

Figure 1. Schematic and data from a tip-hovering experiment. The tip is maintained at fixed distances from the substrate and the lateral motion of the cantilever is monitored. When a bond forms between the tip and the substrate the lateral deflection signal is damped (black line).

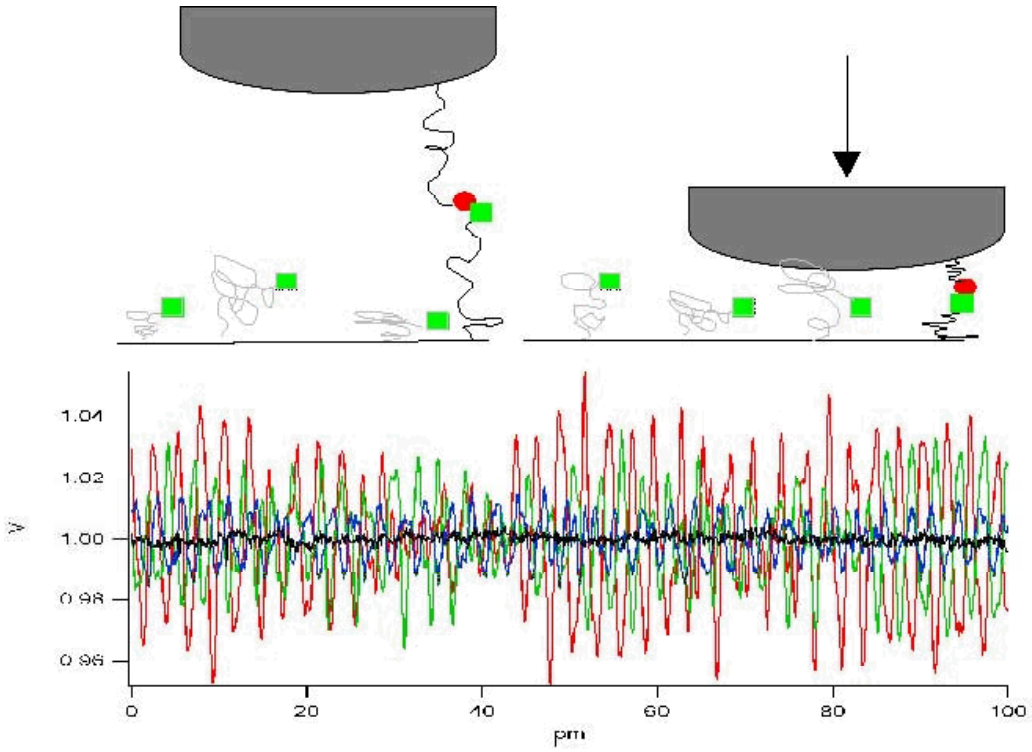

Figure 2. AFM force traces (i.e. force versus distance of the AFM tip from the surface) showing polymer extensions in non-polar solvents. The black line represents a polymer extension in water (i.e. a polar solvent). Because the polymer chains are much stiffer in non-polar solvents, the force required to extend the polymer is much higher. Due to the stochastic nature of bond strength each bond ruptures under a slightly different applied load and different polymer extension.